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Konstantinos Kontomaris

DuPont Fluorochemicals, United States of America, Konstantinos.Kontomaris@DuPont.com

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HFO-1336mzz-Z: High Temperature Chemical Stability and Use as A Working Fluid in Organic Rankine Cycles

Konstantinos (Kostas) KONTOMARIS

DuPont Fluorochemicals R&D,
Wilmington, Delaware, USA
Konstantinos.Kontomaris@DuPont.com

ABSTRACT

Regulatory pressure has been mounting globally to address the issue of climate change. Hydrofluorocarbons (HFCs) with high global warming potentials (GWPs), used as working fluids across many applications, are coming under increasing scrutiny because they are forecast to become significant contributors to global warming in the future. Therefore, there is a need for low GWP working fluids for many applications for which HFCs have been historically preferred. This paper evaluates a new developmental refrigerant, Hydro-Fluoro-Olefin HFO-1336mzz-Z ($\text{cis-CF}_3\text{CH=CHCF}_3$), as a potential working fluid for Organic Rankine Cycles (ORC). It has a favorable toxicity profile based on testing to date and it is non-flammable at both 60 °C and 100 °C. It offers both non-flammability and a very low one-hundred year GWP of 2, thus discrediting an early stereotype about fluids based on HFOs. Even more surprisingly, HFO-1336mzz-Z remained chemically stable in the presence of carbon steel, copper, aluminum, air and moisture up to the maximum temperature tested of 250°C despite its unsaturated chemical nature. It also remained stable to stereo-isomerization in the presence of carbon steel, copper and aluminum at 250°C despite the thermodynamic driving force for isomerization to the more energetically favored HFO-133mzz-E isomer. The stability of HFO-1336mzz-Z was found to be significantly higher than other saturated and unsaturated working fluids. HFO-1336mzz-Z has a normal boiling point of 33.4°C and a relatively high critical temperature of 171.3 °C, which result in relatively low vapor pressures and high cycle energy efficiencies. The performance of HFO-1336mzz-Z in subcritical and transcritical power cycles at conditions representative of potential applications was evaluated through computational modeling. Subcritical Rankine cycles with recuperators operating between an evaporating temperature of 160 °C and a condensing temperature of 25 °C with HFO-1336mzz-Z could reach net cycle efficiencies of 25%. HFO-1336mzz-Z could enable more environmentally sustainable ORC platforms to generate power from available heat at higher temperatures and with higher energy efficiencies than incumbent working fluids.

1. INTRODUCTION

Increasing energy prices and a growing awareness of the environmental impacts, in general, and the threat to the earth's climate, in particular, from the use of fossil fuels and associated greenhouse gas emissions are motivating an expanding utilization of relatively low temperature heat (i.e. heat at temperatures lower than about 300 °C). One promising approach is the conversion of low temperature heat to mechanical or electrical power through Organic Rankine Cycles. Low temperature heat may be recovered from various commercial or industrial operations or from mobile or stationary internal combustion engines, can be extracted from geothermal or hydrothermal reservoirs or can be generated through solar collectors.

It is widely recognized that the choice of working fluid (also referred to as the “refrigerant”) plays a critical role in determining the attractiveness of an ORC application. Chemical stability at the intended operating temperatures is a key requirement that a working fluid for an ORC must meet. Chemical stability of a working fluid at high temperatures would allow a more effective utilization of available heat sources. Moreover, low Global Warming Potential (GWP) has been recently added to the list of specifications that a working fluid must meet, especially given that climate protection is a primary motivation for low temperature heat utilization. The availability of a

suitable working fluid with a GWP sufficiently low so as to minimize any business risks from climate protection regulations emerging around the globe is a prerequisite for substantial ORC research and development investments.

The class of low GWP compounds, known as Hydro-Fluoro-Olefins (HFOs), has been emerging as a new generation of refrigerants. For example, HFO-1234yf has been commercialized for automotive air-conditioning applications. Various HFO-based refrigerants are now explored for stationary air conditioning and refrigeration applications. The presence of a double bond in HFO molecules accelerates the atmospheric degradation of HFOs and reduces their atmospheric lifetime, thereby reducing their GWP. Considering HFOs as refrigerants required a paradigm shift because the conventional wisdom had been that unsaturated fluorocarbons were necessarily reactive and, therefore, insufficiently stable to be used as refrigerants. In fact, several HFOs have been found that decompose rapidly in the atmosphere so as to have minimal GWPs but at the same time remain sufficiently stable in refrigeration and air-conditioning systems.

HFO-1336mzz-Z (cis-1,1,1,4,4,4-hexafluoro-2-butene, cis-CF₃CH=CHCF₃), previously also referred to as DR-2, has been recently introduced as a developmental working fluid for various applications including air conditioning chillers (Kontomaris 2010, 2011b, 2011c, 2012a, 2012b), high temperature heat pumps (Kontomaris 2011c, 2011d, 2012b, 2012c, 2012d, 2013a, 2013b; Kontomaris and Leck, 2011) and ORCs (Kontomaris 2011a, 2011c, 2012b, 2012d; Datla and Brasz, 2012; Kontomaris et al. 2013; Minor et al. 2014; Molés et al. 2014). Figure 1 shows the molecular structure of both stereoisomers of HFO-1336mzz.

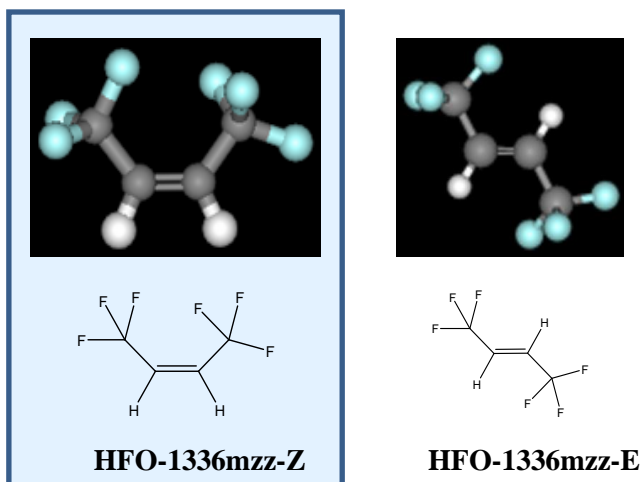


Figure 1: Molecular structure of the two stereoisomers of HFO-1336mzz

The remarkable chemical stability of HFO-1336mzz-Z at 250 °C, despite its unsaturated chemical nature, was first reported by Kontomaris (2011a). The objectives of this paper are to: i) report more recent evaluations of the chemical stability of HFO-1336mzz-Z over a wider range of conditions and compare the stability of HFO-1336mzz-Z to that of other fluids under consideration as working fluids for ORCs; ii) present a comprehensive set of HFO-1336mzz-Z thermodynamic properties; iii) exemplify the performance of HFO-1336mzz-Z in ORCs at operating conditions representative of potential applications.

2. SAFETY, HEALTH AND ENVIRONMENTAL PROPERTIES

Table 1 compares key safety, health and environmental characteristics of HFO-1336mzz-Z to those of a familiar reference fluid that has been used for ORCs, HFC-245fa. HFO-1336mzz-Z is non-flammable at 60 °C and at 100°C according to ASTM E 681-04. This test is used according to ASHRAE Standard 34-2010 to determine the flammability of refrigerants which operate in cooling and heating cycles (involving compression, expansion, evaporation and condensation) similar to Rankine power cycles. Many of the refrigerants evaluated by ASHRAE

have also been under consideration as working fluids for ORCs. The GWP (with 100 year integrated time horizon) of HFO-1336mzz-Z is 99.8 % lower than that of HFC-245fa.

Table 1: Safety, health and environmental properties of HFO-1336mzz-Z and HFC-245fa

	HFC-245fa	HFO-1336mzz-Z
	$\text{CHF}_2\text{CH}_2\text{CF}_3$	$\text{CF}_3\text{CH}=\text{CHCF}_3(\text{Z})$
IUPAC name	1,1,1,3,3-pentafluoro-propane	(Z)-1,1,1,4,4,4-hexafluoro-2-butene
Mol. w. (kg/kmol)	134.05	164.056
Occupational Exposure Limit (ppmv)	300 ⁽¹⁾	500 ⁽²⁾
Flammability	Non-flammable ⁽¹⁾	Non-flammable ⁽³⁾
Safety Class ⁽⁴⁾	B1 ⁽¹⁾	A1 ⁽⁵⁾
Atmospheric Lifetime (yr)	7.7 ⁽⁶⁾	0.060274 (22 days ⁽⁶⁾)
Ozone Depletion Potential	None	None
Global Warming Potential (100 year Integrated Time Horizon)	858 ⁽⁶⁾	2 ⁽⁶⁾

(1) Calm and Hourahan (2007); (2) DuPont Allowable Exposure Limit (AEL); (3) At 60 °C and 100 °C according to ASTM E681-2004; (4) ASHRAE Standard 34-2010; (5) Not established, but meets criteria of A1; (6) Myhre et al. (2013)

3. THERMODYNAMIC PROPERTIES

Table 2 compares key thermodynamic properties of HFO-1336mzz-Z to HFC-245fa. HFO-1336mzz-Z has a higher critical temperature and a lower critical pressure. Figure 2 compares the HFO-1336mzz-Z vapor pressure to HFC-245fa. The slopes of the vapor pressure curves increase with temperature. HFO-1336mzz-Z generates substantially lower pressures than HFC-245fa that may allow higher operating temperatures without exceeding the maximum permissible working pressure of some equipment. Figure 3 compares the HFO-1336mzz-Z temperature-entropy diagram to HFC-245fa. The slopes, dT/ds , of the saturated vapor curves are positive for temperatures in the range from about -10 °C to 150 °C for HFO-1336mzz-Z and from about 0 °C to 130 °C for HFC-245fa. For evaporating temperatures within the above temperature ranges no vapor superheat is required at the expander inlet to ensure dry conditions throughout the expansion step regardless of the expander efficiency. However, some degree of vapor superheat would usually still be specified for practical cycles to protect the expander from unintentional entrainment and carryover of liquid droplets due to non-uniform or fluctuating evaporator conditions. Figure 4 shows the HFO-1336mzz-Z pressure-enthalpy diagram.

Table 2: Thermophysical properties of HFO-1336mzz-Z compared to HFC-245fa

	HFC-245fa	HFO-1336mzz-Z
Normal Boiling Point °C	15.1 ⁽¹⁾	33.4
Critical Temperature °C	154 ⁽¹⁾	171.3
Critical Pressure MPa	3.65 ⁽¹⁾	2.9
Freezing Point °C	-107 ⁽²⁾	-90.5 ⁽³⁾

(1) Calm and Hourahan (2007); (2) Honeywell product literature; (3) Henne and Finnegan (1949)

4. CHEMICAL STABILITY

The surprising chemical stability of HFO-1336mzz-Z at high temperatures, despite its unsaturated chemical nature, was first reported in a patent application by Kontomaris (2011a). The formation of fluoride ion or other unknown products in sealed glass tube tests, carried out according to ASHRAE Standard 97-2007, was negligible even after exposure of HFO-1336mzz-Z to 250 °C for fourteen days in the presence of carbon steel, copper and aluminum. The fluoride ion concentration can be interpreted as an indicator of the degree of HFO-1336mzz-Z degradation.

Subsequent work established the reproducibility of the original HFO-1336mzz-Z chemical stability findings and examined the effect of air and moisture that could occasionally infiltrate power generation and other equipment (Kontomaris, 2013a). The testing procedure was modified to allow air addition to a test tube to a selected pressure after the contents of the tube were frozen with liquid nitrogen and tube headspace was evacuated fully; the glass tube was then sealed by torch. Test results are summarized in Table 3. The air pressure in the headspace of the test tubes was controlled at 7.6 mm Hg and the liquid sample moisture was adjusted to 200 ppm. HFO-1336mzz-Z remained largely stable after exposure to 250 °C in the presence of air, moisture, carbon steel, copper and aluminum for seven days as indicated by the minimal concentration of fluoride ion. Moreover, visual inspections of the tubes and coupons after aging showed no liquid or metal discoloration, insoluble residues or other signs of degradation.

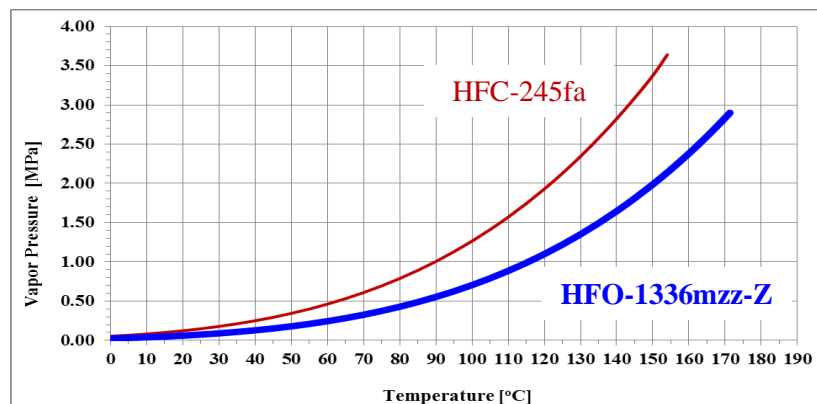


Figure 2: HFO-1336mzz-Z vapor pressure compared to HFC-245fa

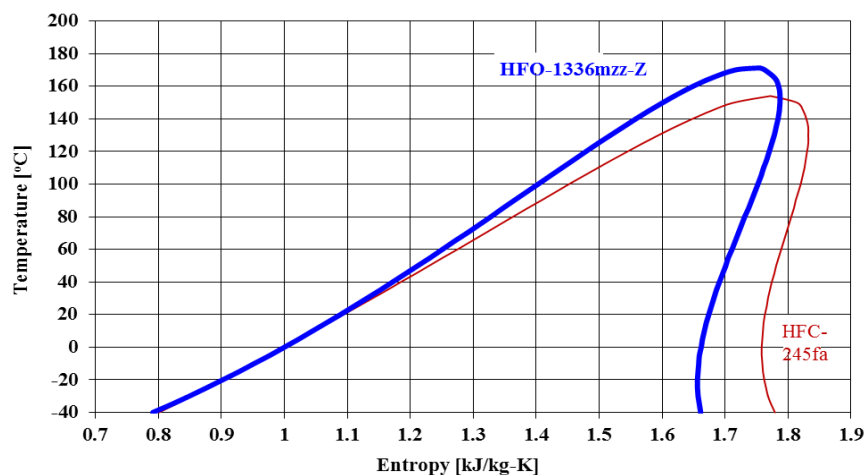


Figure 3: HFO-1336mzz-Z temperature-entropy diagram compared to HFC-245fa

Recent work compared the chemical stability of HFO-1336mzz-Z to that of other incumbent and candidate working fluids (Kontomaris 2013b; Kontomaris et al. 2013). Table 3 indicates that the thermal, oxidative and hydrolytic stability of HFO-1336mzz-Z are comparable to HFC-245fa, a saturated hydro-fluorocarbon that has been used for high temperature applications. The stability of HFO-1336mzz-Z (and HFC-245fa) is superior to that of HCFO-1233zd-E ($\text{E-CF}_3\text{CH=CHCl}$; E-1-Chloro-3,3,3- trifluoroprop-1-ene), a low GWP candidate of recent interest.

Stereo-isomerization of HFO-1336mzz-Z to HFO-1336mzz-E is thermodynamically favoured due to the lower molecular energy of the E (or trans) isomer by about 5 kcal/mole. Remarkably, Table 4 indicates negligible

measured HFO-1336mzz-E concentrations in glass tubes originally containing neat HFO-1336mzz-Z after aging at 175 °C and 200 °C for fourteen days in the presence of carbon steel, copper and aluminum. In contrast, significant stereo-isomerization of HCFO-1233zd-E to HCFO-1233zd-Z is observed under the testing conditions in Table 4. The difference in stereo-isomerization rates between HFO-1336mzz-Z and HCFO-1233zd-E becomes even more dramatic at 250 °C as shown in Figure 5. Apparently, stereo-isomerization of HFO-1336mzz-Z is kinetically hindered.

Table 3: Concentrations (by Ion Chromatography) of fluoride and chloride ions in glass test tubes containing HFO-1336mzz-Z or HFC-245fa or HCFO-1233zd-E after aging at 250 °C in the presence of carbon steel, copper and aluminum coupons for seven days

		Without Air or Moisture Contamination			With Air and Moisture Contamination		
		HFC-245fa	HCFO-1233zd-E	HFO-1336mzz-Z	HFC-245fa	HCFO-1233zd-E ^(*)	HFO-1336mzz-Z
Air	mm Hg	n/a	n/a	n/a	7.6	n/a	7.6
H ₂ O	ppm	n/a	n/a	n/a	200	n/a	200
F ⁻	ppm	8	118	8	20	n/a	11
Cl ⁻	ppm	n/a	530	n/a	n/a	n/a	n/a

(*)Not tested given its high reactivity even in the absence of air and moisture

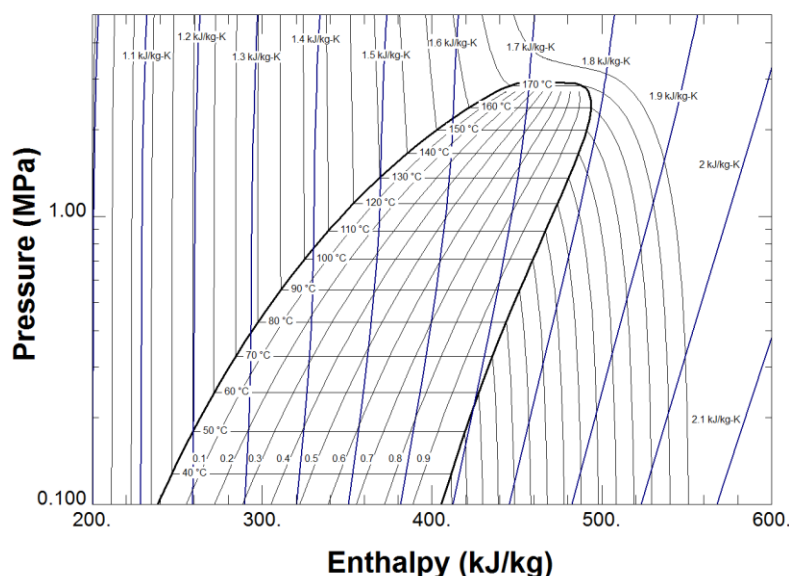


Figure 4: HFO-1336mzz-Z pressure-enthalpy diagram

Table 4: Concentrations (by GC-MS peak area) of HFO-1336mzz-E or HCFO-1233zd-Z in glass test tubes originally containing neat HFO-1336mzz-Z or HCFO-1233zd-E, respectively, after aging at 175 °C and 200 °C in the presence of carbon steel, copper and aluminum coupons for fourteen days

Aging Temp	HFO-1336mzz-E	HCFO-1233zd-Z
°C	wt%	wt%
Stock before aging	Not present	0.02
175	0.004	6.49
200	0.011	8.78

Finally, the thermal stability of HFO-1336mzz-Z at the conditions of Table 3 was compared to three additional working fluids representing different chemical families: HCFC-123 (CHCl_2CF_3), HFE-449sl ($\text{C}_4\text{F}_9\text{OCH}_3$ or HFE-7100) and PEIK ($\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ or Perfluoro Ethyl Isopropyl Ketone or Novec 649). Evidence of fluid degradation (e.g. liquid and metal coupon discoloration) was apparent upon visual inspection of the glass tubes with HCFC-123, HFE-449sl and PEIK after aging. Even higher concentrations of fluoride ion (and chloride ion in the case of HCFC-123) were measured with HCFC-123, HFE-449sl and PEIK than the values in Table 3 (Kontomaris 2013b; Kontomaris et al 2013; Minor et al. 2014).

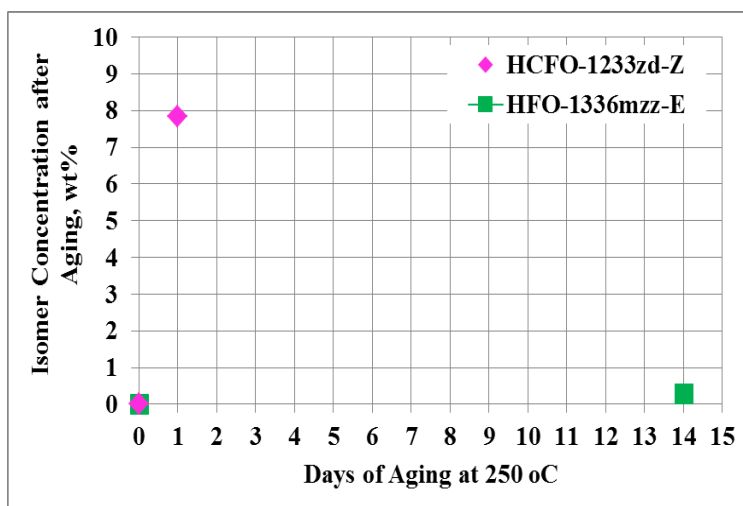


Figure 5: Concentrations (by GC-MS peak area) of HFO-1336mzz-E or HCFO-1233zd-Z in glass test tubes originally containing neat HFO-1336mzz-Z or HCFO-1233zd-E, respectively, after aging at 250 °C in the presence of carbon steel, copper and aluminum coupons

5. CYCLE PERFORMANCE

The design of an ORC system involves many considerations including the characteristics (e.g. entering and leaving temperatures) of the available heat source and sink and the properties of the working fluid the choice of which is informed and constrained by factors beyond its thermodynamic performance (Quoilin et al. 2013); it is beyond the scope of this paper. This section only presents the calculated performance of HFO-1336mzz-Z in representative ORCs to reveal the thermodynamic nature of HFO-1336mzz-Z and ranges of operating conditions for which HFO-1336mzz-Z may prove suitable.

Datla and Brasz (2012) evaluated HFO-1336mzz-Z as a working fluid for an ORC application driven by a heat source with entering and leaving temperatures of 100 °C and 80 °C, respectively. They found good performance. Molés et al. (2014) evaluated HFO-1336mzz-Z as a working fluid for ORCs with evaporating temperatures ranging from 96.85 °C to 146.85 °C and condensing temperatures ranging from 26.85 °C to 76.85 °C and found attractive performance. HFO-1336mzz-Z would require about 36.5% to 41% lower pump power than HFC-245fa to generate a target net power output from a suitable heat source over the range of conditions examined by Molés et al. It would realize net thermal energy efficiencies up to 12% or 17% higher than HFC-245fa for cycles without or with a recuperator, respectively. HFO-1336mzz-Z would require 30.9% to 41.5% larger turbines than HFC-245fa. The net cycle efficiency with HFO-1336mzz-Z increases relative to HFC-245fa with increasing evaporating or condensing temperature. The required turbine size with HFO-1336mzz-Z decreases relative to HFC-245fa with increasing condensing temperature.

A working fluid for subcritical ORC applications is, generally, considered most advantageous for utilizing heat sources at temperatures not much lower than its critical temperature, especially when equipment size and cost are considered. For example, Table 5 summarizes the predicted performance of exemplary Rankine power cycles

without recuperators operating with HFO-1336mzz-Z as the working fluid at the following conditions: evaporating temperature: 160 °C; net power output: 500 kw; liquid sub-cooling at condenser exit: 0 K; expander isentropic efficiency: 85%; and liquid pump isentropic efficiency: 65%. The availability of suitable heat sources and sinks is assumed.

Column A in Table 5 shows the performance of a cycle with no vapor superheat at the expander inlet and a condensing temperature of 75 °C. The condensing temperature in ORC applications can be significantly lower than 75 °C when a low temperature condenser cooling medium is available (e.g. 15 °C water from a natural source or 40 °C water from a cooling tower) and maximum heat recovery from the heat source is a primary objective. The condensing temperature in ORC applications can also be higher than 75 °C (e.g. when cogeneration of hot water for district heating is an objective). Even at an evaporating temperature as high as 160 °C the evaporating pressure, 2.38 MPa remains easy to confine. The volumetric flow rate ratio across the expander, 9.53, exceeds the range of most commonly available positive displacement expanders. The pump consumes a significant fraction, 12.25%, of the power generated by the expander. The net thermal cycle efficiency is 11.07%

Table 5: HFO-1336mzz-E performance in exemplary Rankine power cycles without recuperators; evaporating temperature: 160 °C; net power output: 500 kw; liquid sub-cooling at condenser exit: 0 K; expander isentropic efficiency: 85%; liquid pump isentropic efficiency: 65%

		A	B	C	B vs A %	C vs B %
Vapor Superheat at Evapor. Exit/Expander Inlet	K	0	50	50		
Condenser Saturation Temperature	C	75	75	25		
Temp Lift (Condenser to Evaporator)	K	85	85	135		
Evaporator Pressure	MPa	2.38	2.38	2.38		
Condenser Pressure	MPa	0.37	0.37	0.07		
Pressure Ratio Across Expander	-	6.35	6.35	32.20		
Total Heat Received per Kg in Evaporator	kJ/kg	191.9	263.3	327.5	37.2	24.4
Total Heat Rate to Evaporator	kJ/s	4,517	4,570	2,887	1.2	-36.8
Work from Expander	kJ/kg	24.20	31.77	59.76	31.3	88.1
Vapor Density at Expander Outlet	kg/m ³	21.63	17.88	3.65	-17.4	-79.6
Volumetric Flow Rate at Expander Inlet	m ³ /s	0.11	0.14	0.07	20.9	-49.2
Volumetric Flow Rate at Expander Outlet	m ³ /s	1.09	0.97	2.42	-10.8	149.1
Ratio of Volumetric Flow Rate Across Expander	-	9.53	7.04	34.51	-26.2	390.4
Vapor De-superheating	kJ/kg	25.3	89.1	101.5	252.3	13.9
Total Heat Rejected At Condenser per Kg	kJ/kg	170.6	234.4	270.7	37.4	15.5
Rate of Heat Rejection from Condenser	kJ/s	4,017	4,070	2,387	1.3	-41.4
Work Consumption by Pump	kJ/kg	2.97	2.97	3.04	0.0	2.6
Pump Work as a % of Expander Work	%	12.25	9.34	5.09	-23.8	-45.4
Net Work Output	kJ/kg	21.24	28.80	56.72	35.6	96.9
Mass Flow Rate	kg/s	23.54	17.36	8.82	-26.3	-49.2
Volumetric Capacity for Power Generation	kJ/m ³	459.44	515.01	206.78	12.1	-59.8
Cycle Thermal Efficiency	%	11.07	10.94	17.32	-1.1	58.3
Cycle Thermal Effic. as a % of Carnot Efficiency	%	56.40	55.76	55.58	-1.1	-0.3

Column B in Table 5 shows the predicted performance of a cycle at conditions identical to Column A except at a higher vapor superheat at the evaporator exit (or expander inlet) of 50 K. Vapor superheating would occur with lower heat transfer coefficients than evaporative heating and would require additional heat exchange area. The

higher superheat results in 37.2% higher heat extraction at the evaporator and 31.3% more power generated at the expander per unit mass of fluid. The volumetric flow rate ratio across the expander is reduced by 26.2% to 7.04. The amount of heat rejected at the condenser to desuperheat the vapor entering from the expander is 38% of the total heat rejected at the condenser per unit of fluid mass. The cycle thermal efficiency remains about 11%.

Column C in Table 5 shows the predicted performance of a cycle at conditions identical to Column B except at a lower condensing temperature of 25 °C. The larger difference between condensing and evaporating temperatures for case C, 135 °C, relative to case B, 85 °C, results in 24.4% more heat extracted from the source and 88.1% more power delivered at the expander per unit of fluid mass. Since the power consumed by the pump remains approximately constant, conditions C lead to 96.9% higher net power extracted from the cycle and 49.2% lower required mass flow rate to deliver the nominal cycle power capacity of 500 kw. The evaporator and condenser duties are reduced by 36.8% by 41.4%, respectively. The net cycle efficiency is increased by 58.3% to 17.32%. However, the vapor density at the lower temperature at the expander exit decreases by 79.6% and the ratio of volumetric flow rates across the expander, 34.51, would probably require multi-stage turbine expansion (or a cascade configuration). The amount of heat rejected at the condenser to desuperheat the vapor entering from the expander under conditions C remains about 38% of the total heat rejected at the condenser per kg of fluid.

If a recuperator were added to the cycle to reduce the superheated vapor exiting the expander to its saturation point and transfer all of the extracted heat to preheat the liquid on its way from the pump to the evaporator, the net cycle efficiency would be 25.1% (80.5% of the Carnot efficiency) or 44.9% higher than case C (at the same conditions without a recuperator). The addition of the recuperator also reduces the evaporator and condenser duties by 31% and 37.5, respectively, relative to case C.

6. DISCUSSION AND CONCLUSIONS

HFO-1336mzz-Z is non-flammable at both 60 °C and 100 °C, in contrast to HFO-1234yf and HFO-1234ze-E, the first commercially available HFOs. Non-flammability is clearly mandatory in many ORC applications. However, it is also of great value in reducing the flammability risk and the cost associated with flammability mitigation measures in installations where other flammable materials are necessarily present and can be handled.

HFO-1336mzz-Z was demonstrated to be chemically stable at high temperatures despite its unsaturated chemical nature. HFO-1336mzz-Z remained largely stable to decomposition (de-hydrofluorination), polymerization, oxidation, hydrolysis and structural and positional isomerization in the presence of carbon steel, copper and aluminum up to the maximum temperature tested of 250 °C. Stability to isomerization can be of critical importance when the isomers differ significantly in key properties (e.g. boiling point, toxicity, etc.). The chemical properties of HFO-1336mzz-Z solidify the paradigm shift away from the conventional wisdom that the double bond in fluoro-olefins is necessarily unacceptably reactive for use as working fluids.

HFO-1336mzz-Z and HFC-245fa showed the highest thermal stability at 250 °C among various compounds tested (HCFC-123, HCFO-1233zd-E, HFE-449sl and PEIK). Compounds containing chlorine in their molecules (e.g. HCFO-1233zd-E and HCFC-123) or ether linkages showed substantially reduced chemical stability. HFO-1336mzz-Z and HFC-245fa showed comparable stability; however, HFO-1336mzz-Z provides the highest thermal stability with the lowest GWP (99.8 % reduction vs. HFC-245fa).

The relatively high critical temperature, low vapor pressure and high thermal stability of HFO-1336mzz-Z make it particularly suitable for ORC applications for which a heat source is available at relatively high temperatures (e.g. exhaust gases from a stationary or mobile internal combustion engine) thus resulting in high cycle energy efficiencies. Moreover, the efficiency of ORCs with HFO-1336mzz-Z would be benefited from the use of recuperators. For example, an ORC with a recuperator operating with HFO-1336mzz-Z between 25 °C and 160 °C could realize an attractive net cycle efficiency of about 25%.

The advantages of transcritical Rankine cycles in matching the temperature profiles of non-isothermal heat sources and increasing cycle efficiencies and have been discussed extensively in the literature (Schuster et al. 2010). The chemical stability of HFO-1336mzz-Z at temperatures higher than its critical temperature could enable trans-critical

ORC cycles resulting in higher cycle efficiencies. For example, a transcritical ORC without a recuperator operating with HFO-1336mzz-Z at 210 °C and 4 MPa at the expander inlet and a condensing temperature of 75 °C would result in a cycle energy efficiency of 12.7% (assuming the same expander and pump efficiencies as in Table 5). The resulting cycle efficiency would be 16.1% higher than the efficiency of a subcritical cycle with the same temperature at the expander inlet (Table 5, Column B). Moreover, the heat exchanger duties would be about 14% lower for the transcritical cycle relative to cycle B. The vapor exiting the expander would have a relatively high temperature of 134 °C, suitable for recuperation or heating duty to further enhance the efficiency in using the available heat at 210 °C for either power generation or heating. The net cycle efficiency of transcritical cycles increases with increasing expander inlet temperature and pressure; for example, it can reach 13.9% at 275 °C and 6 MPa at the expander inlet (without recuperation, 75 °C condensing temperature and expander and pump efficiencies same as in Table 5).

HFO-1336mzz-Z could enable more environmentally sustainable power generation platforms to meet sustainability objectives (e.g. reducing non-renewable energy consumption and greenhouse gas emissions) with attractive economics. It is currently under lab and field testing for various targeted applications.

ACKNOWLEDGEMENT

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